



# Promoting the activity of Ce-incorporated MOR in dimethyl ether carbonylation through tailoring the distribution of Brønsted acids

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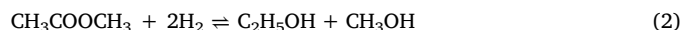
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## ABSTRACT

As Brønsted acid site (BAS) located in 8-membered ring (8-MR) of zeolite is accepted as the exclusive active site for dimethyl ether carbonylation to methyl acetate, tailoring the distribution of tetrahedral Al in zeolite channels is important to improve catalytic performance. In this work, a series of Ce-containing mordenite were synthesized by one-step hydrothermal method. By a combination of mutually complementary characterization techniques (e.g. XPS, UV-vis, Raman, acidity characterizations etc.), it is confirmed that Ce atoms incorporated into the zeolite framework as Ce<sup>3+</sup> species, resulting in an enrichment of BAS in the 8-MR. Acid strength, apparent activation energy and DFT calculations revealed that the incorporation of Ce resulted in an increase of Si-OH-Al in the 8-MR, which was responsible for the improved activity. This work provides a facile way to tailor the acidic concentration and distribution of zeolites, which is able to guide rational design of zeolites for the shape-selective catalysis.

## 1. Introduction

Growing concerns about environment, depletion of oil reserves, and energy security have pushed the topic of energy to the center stage. In order to reduce the reliance on imported crude oil, searching for alternatives to petroleum-derived fuels and chemicals for many countries has gained momentum in past decades. In the context, ethanol as a potential alternative synthetic fuel has attracted tremendous interests [1–3]. Recently, a new route of ethanol production has been developed, which relies on transformation of the carbon source (such as coal, biomass) into syngas [4–7]. This process is an integrated technology consisting of carbonylation of dimethyl ether (DME) to form methyl acetate (MA) and the subsequent hydrogenation to yield ethanol (Eqs. (1) and (2)), both of which shows appreciable selectivity. The main byproduct methanol can be recycled to produce DME by dehydration. Furthermore, the absence of ethanol-water binary azeotrope in products significantly reduces separation cost. Therefore, the advantages of high atom economy, low energy consumption and few emissions make this route promising and competitive in industry.



As a key step in conversion of syngas to ethanol, the carbonylation of DME to MA is usually catalysed by solid acid catalysts such as zeolites and heteropoly acids (HPAs) [8–10]. Compared with HPAs, zeolites show favourable activity and selectivity due to confinement effect of well-defined structure. Zeolite catalyzed DME carbonylation reaction is proved to be a typical spatially confined reaction on Brønsted acid sites [5,10,11]. The catalytic performance strongly depends on the structure of zeolite framework and the distribution of Brønsted acid site [12,13]. Mordenite (MOR) has been demonstrated as an outstanding candidate to catalyze this reaction, which contains a main channel with 12-membered ring (12-MR,  $6.7 \times 7.0 \text{ \AA}$ ) along the [0 0 1] direction and an 8-membered ring side pockets (8-MR,  $3.4 \times 4.8 \text{ \AA}$ ) in the [0 1 0] direction [14]. The 8-MR channels that surround catalytically active Brønsted acid sites confine reactive intermediates in dimensions, imparting shape-selective properties that facilitate MA formation. In contrast, the 12-MR with larger voids is prone to the coke deposit [15–17]. Therefore, it is anticipated that modulating the distribution of framework Al to selectively concentrating the Brønsted acid site within 8-MR is an efficient strategy to improve the yield of MA, even if it is still

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a quite challenging task.

To date, several approaches have aimed at tailoring the Brønsted acidity in aluminosilicate zeolite. Post-synthesis modifications in acidic/alkaline media or steam are extensively investigated for introducing or removing tetrahedral  $\text{AlO}_4$  units to modify the acidity [18–20]. However, they tend to give rise to associated drawbacks, such as the deterioration of crystallinity, the blockage of channels and the shield of acid sites. Modification of hydrothermal synthesis by manipulating Si and Al composition and choosing an appropriate organic structure directing agent are also capable to induce non-random distribution of framework Al ( $\text{Al}_\text{F}$ ) atoms [21–24]. Recently, growing interest is focused on the heteroatom-substitution during one-pot synthesis [25–28]. Compared with the above two methods, it is an effective and controllable way to adjust the Brønsted acid site location corresponding to  $\text{Al}_\text{F}$  siting. Because dislodgement of  $\text{Al}_\text{F}$  atoms among different channels may occur by virtue of the competitive occupancy between  $\text{Al}_\text{F}$  and the heteroatom. Furthermore, the heteroatom composition (e.g.  $\text{Ga}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{B}^{3+}$ ) influences the acid strength [29,30], which plays an important role in the catalytic properties.

In this work, we reported a facile protocol for deliberately regulating H-MOR acidity by heteroatom isomorphous substitution. A series of Ce-containing MOR zeolites were successfully synthesized by one-step hydrothermal method. We endeavored to explore the nature of Ce species as well as the evidence of changes in acidity of the Ce-doped MOR by several complementary characterization techniques. Afterwards, DFT calculations and catalytic evaluations were combined to elucidate the promotion mechanism of Ce modified MOR catalysts.

## 2. Experimental

### 2.1. Synthesis of Ce-incorporated MOR zeolites

The Ce-containing MOR zeolites were synthesized by implementing a one-pot hydrothermal method. The synthesis process as well as key factors in preparation was diagrammatically represented in Fig. S1. Silica source (30 wt.%  $\text{SiO}_2$ ),  $\text{NaAlO}_2$ , NaOH and  $\text{Ce}(\text{NO}_3)_3$  were mixed and stirred at room temperature for 4 h, followed by adding tetraethylammonium hydroxide (TEAOH, 25 wt.%, Guangfu Fine Chemical Co., Ltd.) aqueous solution as the structure-directing agent and commercial MOR (Nankai University catalyst Co., Ltd.) as the seed (1 wt.% relative to  $\text{SiO}_2$ ). The molar composition of the synthesis gel was  $1.0\text{SiO}_2: 0.083\text{NaAlO}_2: 0.2\text{NaOH}: 0.23\text{TEAOH}: n\text{Ce}(\text{NO}_3)_3$  ( $n = 0, 0.01, 0.021, 0.042$ ). The well-mixed gel was stirred for 1.5 h and then crystallized in a Teflon-lined stainless steel autoclave at  $170^\circ\text{C}$  for 3 days. After the reaction, the autoclave was cooled down and the products were filtered, washed with deionized water, dried overnight at  $100^\circ\text{C}$  and calcinated at  $550^\circ\text{C}$ . The temperature for calcination was increased with a ramp of  $1^\circ\text{C}/\text{min}$  from room temperature to  $550^\circ\text{C}$ , then maintained at  $550^\circ\text{C}$  for 5 h, aiming to remove the structure-directing agent completely. The detemplated samples were ion-exchanged with  $\text{NH}_4\text{NO}_3$  (0.2 M) twice at  $80^\circ\text{C}$  for 6 h, then dried overnight at  $100^\circ\text{C}$ , followed by calcination at  $500^\circ\text{C}$  for 4 h with a heating rate of  $2^\circ\text{C}/\text{min}$ . The obtained zeolites were denoted as xCe-M, where x represented the mole percentage of Ce in sum of Ce, Al and Si in the samples determined by ICP-OES.

For reference, a Ce-containing MOR sample was prepared by physical mixing process (see procedure in Fig. S1). The 0Ce-M and Ce ( $\text{NO}_3$ )<sub>3</sub> mixture was milled in a planetary ball mill for 10 h at 160 r/min, and then calcined at  $500^\circ\text{C}$  for 4 h. The prepared sample was labelled as yCe/M, where y represented the mole percentage of Ce in sum of Ce, Al and Si in the sample. Furthermore, another sample without Ce was prepared and labeled as 0Ce-M-BM. The preparation was similar to yCe/M but without the addition of  $\text{Ce}(\text{NO}_3)_3$ .

### 2.2. Catalytic evaluations

The reactions of DME carbonylation to MA were performed in a stainless-steel tubular fixed-bed reactor (8.0 mm i.d.) under 1.5 MPa. Typically, 1 ml of catalyst (~0.5 g, 40–60 mesh) was loaded and pre-treated under  $\text{N}_2$  atmosphere (99.99%, Tianjin Sixon Gas Co., Ltd) at  $200^\circ\text{C}$  for 9 h. The catalytic reaction was initiated by introducing the reactant gases ( $\text{DME}/\text{CO} = 1:49$ , vol.: vol.) with a constant flow rate of 100 ml/min adjusted by a mass flow controller. The reaction conditions (i.e. pressure, ratio of  $\text{DME}/\text{CO}$ ) were chosen in accordance with the previously reported optimized system [7,16]. The products were analysed by a gas chromatograph (Agilent 7890B) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The conversion of DME ( $X_{\text{DME}}$ ), selectivity of MA ( $S_{\text{MA}}$ ) and the space time yield of MA (MA STY) were calculated by using the equations in previous study [31,32]. TOF was calculated on the following equation:

$$\text{TOF (h}^{-1}\text{)} = \frac{\text{Total flow rate of DME (mol/h)} \times X_{\text{DME}}}{m_{\text{cat}}(\text{g}) \times \text{Number of Brønsted acid site in 8-MR (mol/g)}}$$

### 2.3. Characterization

X-ray diffraction (XRD) measurement were carried out using a Rigaku D/max-2500 diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ), operating at 40 kV and 200 mA. The patterns were collected in the range of  $2\theta = 3^\circ\text{--}50^\circ$  with a scanning speed of  $8^\circ/\text{min}$ .

The actual atomic composition of xCe-M zeolites was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (VISTA-MPX, Varian).

Nitrogen adsorption was performed at  $-196^\circ\text{C}$  on a Micromeritics ASAP 2020 instrument to evaluate the textural properties of the catalyst. Prior to conducting the analysis, the samples were outgassed under high vacuum conditions at  $200^\circ\text{C}$  for 24 h in order to remove adsorbed species such as water. The total pore volumes and median pore width were determined by Horvath-Kawazoe (H-K) equation. The micropore surface area and the micropore volume were calculated using the t-plot method.

Diffuse reflectance ultraviolet-visible (UV-vis) spectra were collected using a Shimadzu UV-2550 UV-vis spectrophotometer in the range of 200 nm–600 nm with  $\text{BaSO}_4$  as a reference.

X-ray photoelectron spectroscopy (XPS) was performed by employing a Thermo Fisher ESCALAB 250Xi instrument using monochromatic Al  $\text{K}\alpha$  source ( $h\nu = 1486.6 \text{ eV}$ ) as an X-ray source. Prior to the analysis, the samples were dried at  $110^\circ\text{C}$  for 4 h to remove water and other adsorbed species. An operating power of 150 W and a pass energy of 30.0 eV were applied to scan the energy region of the photoelectrons. All binding energies were calibrated internally by the  $\text{C}1\text{s}$  peak at 284.8 eV. The number of scans for O 1s and Ce 3d are 2 and 8, respectively.

$^{27}\text{Al}$  magic-angle spinning nuclear magnetic resonance ( $^{27}\text{Al}$  MAS NMR) spectra of samples were recorded using a Varian Infinityplus 300 MHz spectrometer operating at a magnetic field of 7.0 T magnet. The experiments were performed at 78.1 MHz using a 4 mm MAS probe at a rate of 8 kHz. The spectra were acquired at ambient temperature from 512 scans with a  $\pi/12$  pulse width of 0.6  $\mu\text{s}$  and a recycle delay of 3 s. Chemical shifts were referenced versus excess aluminium nitrate aqueous solution.

$^{29}\text{Si}$  MAS NMR investigations were recorded by a Bruker Avance III 400WB spectrometer using a 7 mm probe at resonance frequencies of 79.5 MHz. The spectra were measured upon single pulse excitation of  $\pi/2$  for  $^{29}\text{Si}$  with repetition time of 20 s and recorded with sample spinning rate of 4 kHz.

The Fourier transform infrared (FTIR) spectra in the region of framework T–O–T vibration were recorded using a Thermo Scientific Nicolet 6700 apparatus equipped with a DTGS detector. Each spectrum was obtained by averaging 32 scans collected at  $4 \text{ cm}^{-1}$  resolution using KBr as diluent (1 mg sample / 100 mg KBr).

The FTIR spectra of O–H region were recorded a mercury cadmium telluride (MCT) detector. In each experiment, a self-supported wafer (13 mm dia.) made of 20 mg of catalyst was loaded into the *in situ* stainless steel cell equipped with CaF<sub>2</sub> windows and connected to an evacuation system. The catalyst wafer was degassed under a vacuum of 10<sup>−4</sup> Pa and heated at 400 °C for 1 h to completely remove the impurities from the surface of samples. The spectra were obtained at 30 °C at a resolution of 4 cm<sup>−1</sup> by averaging 32 scans. All the FTIR spectra were normalized by the weight of the wafers.

The Raman spectra were taken on a HR Evolution confocal Raman microscope system (HORIBA, France). A 266 nm laser with an X 50 air objective was employed. The Raman signal was acquired using a 2400 lines/mm grating centered between 200 and 1800 cm<sup>−1</sup>. For each spectrum, the acquisition time were 120 s.

NH<sub>3</sub>-TPD experiment was conducted using a Micromeritics Autochem II 2920 instrument equipped with a TCD. In a typical test, 100 mg of the catalyst was loaded in a quartz tube and cleaned by flowing Ar at a rate of 10 ml/min for 1 h at 200 °C. Then the sample was exposed to excess NH<sub>3</sub>, followed by purging with Ar for 1 h at 30 ml/min to remove the physically adsorbed NH<sub>3</sub>. The TPD profiles were recorded from 150 °C to 850 °C at a rate of 10 °C/min under a He flow (30 mL/min).

*In situ* FTIR spectra of alkaline probe molecules (pyridine and NH<sub>3</sub>) adsorption were recorded to quantify the number of Brønsted acid sites in different channels. The background spectrum was collected when the sample was cooled to 150 °C in vacuum. Subsequently, the catalyst was saturated with pyridine or NH<sub>3</sub> for 30 min, and then evacuated to eliminate physically adsorbed molecules. IR spectra were collected in the range of 4000–1100 cm<sup>−1</sup> at a resolution of 4 cm<sup>−1</sup> by averaging 32 scans.

TPD-IR of NH<sub>3</sub> after pyridine saturation was collected on the same facility to exclusively determine the acidic strength of Brønsted acid sites in 8-MR channels. After being saturated by pyridine vapor, the self-supported wafer was exposed to 10% NH<sub>3</sub>/Ar at 150 °C for 30 min, and outgassed in order to remove excess NH<sub>3</sub> in gas phase as well as physisorbed species. Subsequently, the sample was heated at a ramp rate of 10 °C/min to 600 °C under the vacuum condition to allow NH<sub>3</sub> and pyridine desorption, and the spectra were acquired at every 3.3 °C. The differential change of IR intensity with respect to temperature, which originates from desorption of NH<sub>3</sub> within Brønsted acid sites in 8-MR, was calculated based on the intensity of band at 1427 cm<sup>−1</sup>, and the negative value  $-d(I_{1427 \text{ cm}^{-1}})/dT$  reflected the desorption rate of NH<sub>3</sub> [33].

## 2.4. Computational details

Density functional theory (DFT) calculations were performed by using the double numeric quality basis set plus polarization (DNP) implemented in the Dmol<sup>3</sup> program package. The Perdew Wang (PW91) functional was employed throughout all computations. Considering to computational efforts, the core electrons of Ce and Al atoms were replaced by an effect core potentials (EPC) while other atoms were treated in an all-electron basis set. The convergence tolerance of energy, maximum force and maximum displacement were 2 × 10<sup>−5</sup> Ha, 4 × 10<sup>−3</sup> Ha/Å and 5 × 10<sup>−3</sup> Å, respectively. The complete linear synchronous transit (LST) and quadratic synchronous transit (QST) approach were employed to determine the transition state (TS). All the TSs were verified by only one imaginary frequency.

The MOR framework consists of two channels: a large 12-MR and an 8-MR side pocket. The two channels interconnect vertically with each other. In the MOR framework, there are four nonequivalent tetrahedral sites: T2 and T4 sites in the main channel, T3 in the 8-MR and T1 in the network between the 8-MR and 12-MR channels. In this study, a cluster model consisting of 100 tetrahedral sites (shown in Fig. 1a) extracted from the periodic MOR structure was employed to determine the preferred location of Ce<sup>3+</sup> and Al<sup>3+</sup> in MOR. The acidity of Brønsted acid

sites on T3AlO33H and T3CeO33H and the corresponding activation energies for CO insertion (rate-determining step) were also obtained on the 100 tetrahedral sites structure (100 T) (Fig. 1a–c). The acidity and activation energy of O–H in T3AlO33H and T3CeO33H were also obtained based on the 100 tetrahedral sites structure (100 T) (Fig. 1a–c). Note that the adopted model was large enough to enclose the main channel (12-MR) and the side pocket (8-MR) at the center of the structure so as to ensure greater accuracy in DFT calculations. The substitution energies of Si<sup>4+</sup> by Al<sup>3+</sup> (E<sub>subAl</sub>) of the sites around the T1 were calculated based on a 62 tetrahedral sites (62 T) structure with T1 site in the center (Fig. 1e–f). All the next-nearest-neighbor T-sites of T1 were considered. In order to ensure that the local environment of Ce<sup>3+</sup> and Al<sup>3+</sup> center could provide reasonable information, all of the considered substitution sites were at least linked to four –O– (SiO–)<sub>3</sub> groups. The structure was terminated by H atoms located 1.11 Å from the O atoms and orientated toward the Si atoms in the next coordination sphere.

The deprotonation energy (DPE) is defined as the energy required to break the H–O bond on zeolite framework, forming a proton and a zeolite framework anion. An acid site with a large DPE value corresponds to weak acidity. The DPE was calculated using the following formula:

$$E_{\text{DPE}} = E_{\text{Zeo-}} - E_{\text{Zeo-H}}$$

where E<sub>Zeo-</sub> refers to the energy of the zeolite framework without the H<sup>+</sup> and E<sub>Zeo-H</sub> is the energy of a neutral zeolite with Brønsted acid sites.

The substitution energies of Si by Al (E<sub>subAl</sub>) were calculated according to the following equation:

$$E_{\text{subAl}} = E_{\text{Zeo-Al3+}} + E_{\text{Si(OH)4}} - E_{\text{Zeo-Si4+}} - E_{\text{Al(OH)3}} - E_{\text{H2O}}$$

where E<sub>Zeo-Al3+</sub> and E<sub>Zeo-Si4+</sub> are the energies of MOR zeolite after and before Si atom is substituted by heteroatom, respectively. E<sub>Si(OH)4</sub>, E<sub>Al(OH)3</sub> and E<sub>H2O</sub> are energies of corresponding molecules. A lower value of E<sub>subAl</sub> suggests the substitution of Si is preferable.

The E<sub>subAl</sub> difference between T1 site occupied by Al<sup>3+</sup> and Ce<sup>3+</sup> (ΔE<sub>subAl(T1Al-T1Ce)</sub>) was calculated as

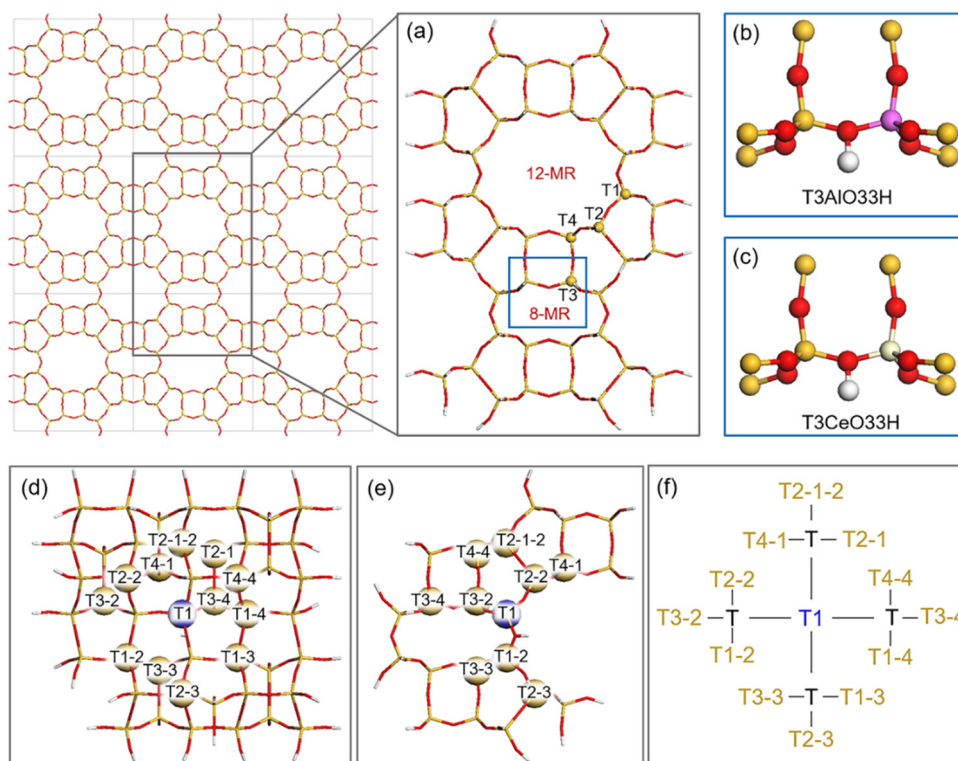
$$\Delta E_{\text{subAl(T1Al-T1Ce)}} = E_{\text{subAl(T1Al)}} - E_{\text{subAl(T1Ce)}}$$

where E<sub>subAl(T1Al)</sub> and E<sub>subAl(T1Ce)</sub> are the E<sub>subAl</sub> when T1 site was occupied by Al<sup>3+</sup> and Ce<sup>3+</sup> respectively. The higher ΔE<sub>subAl(T1Al-T1Ce)</sub> corresponds to an easier substitution of Si<sup>4+</sup> by Al<sup>3+</sup> at NNN T sites.

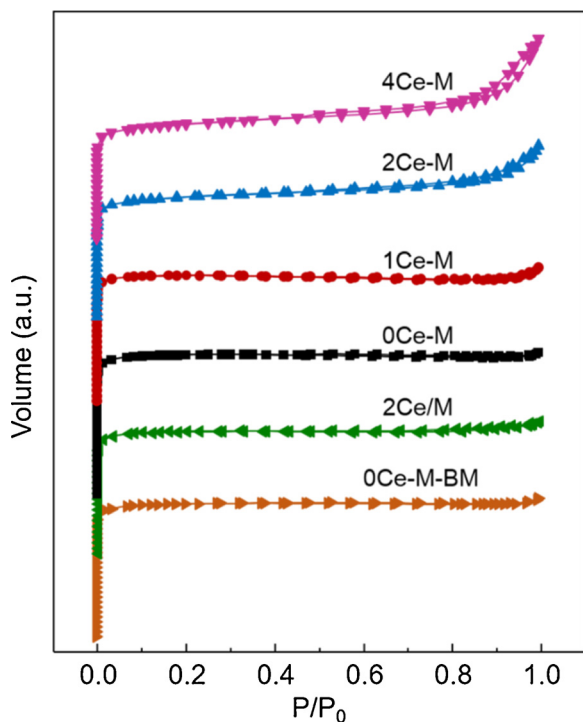
## 3. Results and discussion

### 3.1. Composition and textural properties

The N<sub>2</sub> adsorption-desorption isotherms were recorded to evaluate the porosity of different samples (Fig. 2). According to the IUPAC classification, the xCe-M samples exhibits transformation of isotherms from Type I to a combination of Type I and IV with the increase of Ce content, suggesting that the mesopores are formed by Ce incorporation. The N<sub>2</sub> uptake at P/P<sub>0</sub> < 0.05 indicates that all the samples have microporous structure, and the addition of Ce in the synthesis process does not significantly affect the micropores. The hysteresis loop of the xCe-M is enlarged along with addition of Ce, denoting that these samples have greater external surfaces. The textural properties derived from the N<sub>2</sub> adsorption-desorption isotherm are listed in Table 1. Decreases in micropore surface area and micropore volume with increasing Ce contents in the samples were obtained. This tendency may be attributed to the destruction of the zeolite framework, and/or the occupation of internal space by extra framework species. On the other hand, the mesopore volume and media pore width increase with increasing the Ce content, owing to the creation of structure defects by incorporating Ce ions into the zeolite framework. Compared with 0Ce-M sample, ball milling process (0Ce-M-BM) resulted in a slight decline in micropore surface



**Fig. 1.** (a) Structure of studied 100 T MOR model, (b) enlargement of T3AlO33H site in 100 T MOR model, (c) enlargement of T3CeO33H site in 100 T MOR model, (d) side view and (e) front view of studied 62 T structure, and (f) diagram of the labels in 62 T.



**Fig. 2.** N<sub>2</sub> adsorption and desorption isotherms of samples.

area, due to partial deterioration of zeolite framework. For the 2Ce/M sample, both the surface area and the pore volume are smaller than those of 0Ce-M-BM, indicative of micropores blocking by CeO<sub>x</sub>.

**Table 1**

The textural properties of samples.

Sample	Pore volume (cm <sup>3</sup> ·g <sup>-1</sup> )			Median pore width (nm)	Micropore surface area (m <sup>2</sup> ·g <sup>-1</sup> )
	Total	Micro-	Meso-		
0Ce-M	0.220	0.203	0.017	0.86	436
1Ce-M	0.207	0.190	0.017	0.86	407
2Ce-M	0.263	0.159	0.104	1.04	333
4Ce-M	0.306	0.143	0.163	1.66	307
2Ce/M	0.195	0.179	0.016	0.87	384
0Ce-M-BM	0.207	0.185	0.022	0.87	402

### 3.2. Framework incorporation

The element composition of Ce-incorporated MOR zeolites with different Ce contents as well as the mole percentage of Ce in sum of Ce, Al, and Si (M<sub>Ce</sub>%) are summarized in Table 2. Although the initial Al contents of the raw materials are equivalent in the mixed sol-gel, the actual concentrations of Al and Si in the xCe-M (x = 0, 1, 2) samples are found to decrease with increasing Ce concentration, evidencing the inherent competition between framework T atom (Si and Al) and Ce during the hydrothermal synthesis process. However, when the M<sub>Ce</sub>% reached 4.1%, the amount of both the Al and Si species decrease sharply, which might be caused by the partially collapse of the MOR structure through heteroatoms incorporating into zeolite framework.

Powder XRD was employed to explore the phase composition and refine the unit cell parameters of all samples. Fig. 3a shows the XRD patterns of the xCe-M and ball-milled samples. The typical diffraction peaks associated with MOR zeolites are present for all the xCe-M samples, suggesting that well-crystallized MOR zeolites are obtained in this study. No characteristics of Ce related species are observed, indicative of high dispersion in xCe-M samples. Moreover, one of the strongest peak in the XRD pattern of the MOR zeolite corresponding to the crystal plane of (150) is magnified in Fig. 3b. The peak gradually

**Table 2**  
Chemical composition and unit cell parameters of samples.

Sample	Element content (mmol g <sup>-1</sup> )			$\frac{\text{Ce}}{\text{Ce+Al+Si}}$ (%)	Unit cell parameter			
	Si	Al	Ce		a(Å)	b(Å)	c(Å)	V(Å <sup>3</sup> )
0Ce-M	14.20	1.30	0	0	18.13	20.12	7.46	2722
1Ce-M	14.20	1.27	0.18	1.1	18.22	20.10	7.48	2741
2Ce-M	14.08	1.17	0.33	2.1	18.16	20.32	7.49	2762
4Ce-M	9.85	0.75	0.45	4.1	18.15	20.32	7.49	2761
2Ce/M	14.05	1.29	0.33	2.1	18.13	20.22	7.46	2736
0Ce-M-BM	14.12	1.29	0	0	18.15	20.20	7.46	2735

shifts towards smaller angles with increasing  $M_{\text{Ce}}\%$ , which implies an increase in the unit lattice parameters. Since radius of Ce ion is larger than that of Al and Si ions, the unit lattice parameter is increased upon Ce ions incorporation into the framework of MOR [25,34].

Unlike the case of  $x\text{Ce-M}$  samples, 2Ce/M sample prepared by ball milling presents both of the  $\text{CeO}_2$  and MOR phases. Given the almost identical Ce content in 2Ce-M and 2Ce/M, it is conclusive that one-pot synthesis makes the Ce species well-dispersed on H-MOR, while physical mixing process results in considerable  $\text{CeO}_2$  aggregates, which is supported by TEM images (Fig. S2). The shift in the diffraction peak at  $2\theta = 22.3^\circ$  and the variation of unit cell parameter are not observed, suggesting that the substitution effect is not prompted by physical mixing and the variations in the XRD pattern of  $x\text{Ce-M}$  are not caused by  $\text{CeO}_2$  species.

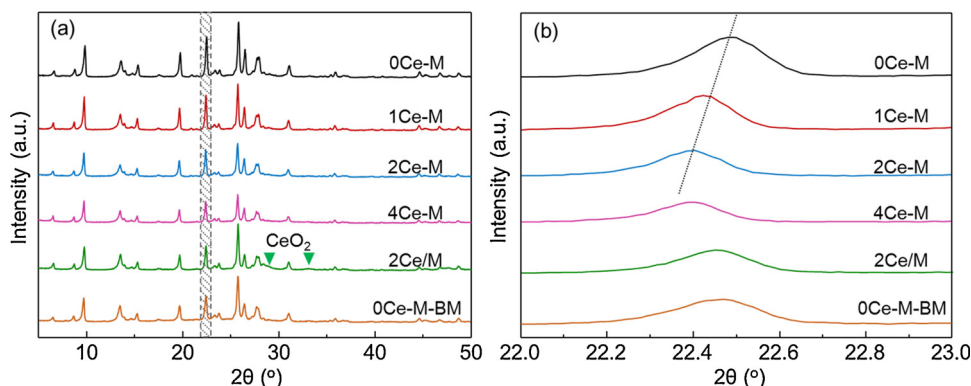
The UV-vis spectra (shown in Fig. 4a) show absorption bands at around 210 nm, attributed to the aluminosilicate matrix [35]. The band at 270 nm, associating with the tetrahedral  $\text{Ce}^{3+}$  in MOR, becomes more intense as the  $M_{\text{Ce}}\%$  increases [25,36]. In addition, an adsorption band at higher than 320 nm emerges as the major band for 2Ce/M and as a shoulder for  $x\text{Ce-M}$ , indicating the coexistence of extraframework  $\text{CeO}_x$  nanocrystallites [37]. It is noteworthy that due to the high dispersion of the extraframework species, the  $\text{CeO}_2$  phase is not identified in the XRD pattern of the  $x\text{Ce-M}$  samples.

The core level XPS spectrum of the O 1s spectrum pertaining to 0Ce-M shows a main peak at 532.4 eV (Fig. 4b), which is attributed to the binding energy (BE) of oxygen in aluminosilicates. With the increment of Ce, the peak progressively shifts to the higher BE side. Generically, a higher BE value indicates a lower electronegativity of adjacent atoms [38]. Considering that the electronegativity of Ce atom (1.12) is much lower than that of Al atom (1.61), the isomorphous substitution of Al by Ce would increase the electron density of the framework oxygen and result in an increase in BE. However, the O 1s BE of 4Ce-M is identical to that of the 2Ce-M, because it is difficult for excess Ce atoms to incorporate into the MOR framework as the  $M_{\text{Ce}}\%$  is higher than 2.1%. Besides, a shoulder at about 530 eV assigned to the oxygen in the  $\text{CeO}_x$  lattice arises in 4Ce-M and 2Ce/M, revealing that the unincorporated Ce species are present as  $\text{CeO}_2$  in 4Ce-M [39].

The FTIR spectra of Ce-incorporated samples in the region of framework T—O—T vibration exhibit all the characteristic bands of MOR zeolite, similar to the 0Ce-M (Fig. 4c). Nevertheless, the band at  $1082\text{ cm}^{-1}$ , due to asymmetric stretching of T—O—T, gradually broadens as the amount of Ce increases, indicating isomorphous substitution by heteroatom in zeolites [40,41]. Notably, the two references (i.e. 2Ce/M and 0Ce-M-BM) also exhibit sharp peak at  $1082\text{ cm}^{-1}$ , verifying that the broadening of T—O—T vibration in  $x\text{Ce-M}$  is caused by incorporation of Ce.

As Raman is a sensitive approach to characterize zeolite textures, it is conducted to explore the effect of Ce addition on the MOR framework (Fig. 4d). The well-resolved bands at  $395$  and  $450\text{ cm}^{-1}$  are assigned to bending mode of 5-membered ring (5-MR) and 4-membered ring (4-MR), respectively [42]. Notably, a red shift of the band at  $395\text{ cm}^{-1}$  is observed upon Ce-incorporated samples, while the other band stays at  $450\text{ cm}^{-1}$ . In MOR framework, 5-MR consists of T1, T2 and T4 site, while 4-MR contains T3 and T4 site [43]. Thus, Ce atoms occupy the T1 and T2 site rather than T3 and T4 sites. Besides, the 2Ce/M and 0Ce-M-BM display the similar Raman spectra as 0Ce-M, suggesting that both extraframework  $\text{CeO}_x$  and ball-milling process show very limited effect on the MOR framework.

The  $^{29}\text{Si}$  MAS NMR spectra of 0Ce-M, 2Ce-M, 2Ce/M exhibit four overlapped peaks (Fig. 5). The peaks between  $-100$  ppm and  $-120$  ppm are attributed to Q4 [Si(0 M)] site. The peaks at  $-105$  ppm and  $-100$  ppm are assigned to Q3 [Si(1 M)] and Q2 [Si(2 M)] site, respectively [44]. The peaks of Q2 and Q3 sites in 2Ce-M shift to upfield relative to those of 0Ce-M, indicating that the Ce has successfully incorporated into zeolite framework during one-step hydrothermal process [25,45]. Besides, the positions of Q4 peaks stay at  $-112.2$  ppm and  $-113.3$  ppm for all the samples, that is to say, the chemical environment of Si(0 M) is not influenced by heteroatoms. Note that no peak shift is observed in ball-milled sample (2Ce/M), comparing with 0Ce-M. These observations imply that the  $\text{CeO}_x$  species do not affect the peak position and confirms that the upfield shift of Q2 and Q3 peaks in 2Ce-M is definitely caused by the Ce incorporation.



**Fig. 3.** (a) XRD patterns of samples and (b) enlarged scale between  $2\theta = 22.0^\circ - 23.0^\circ$ .

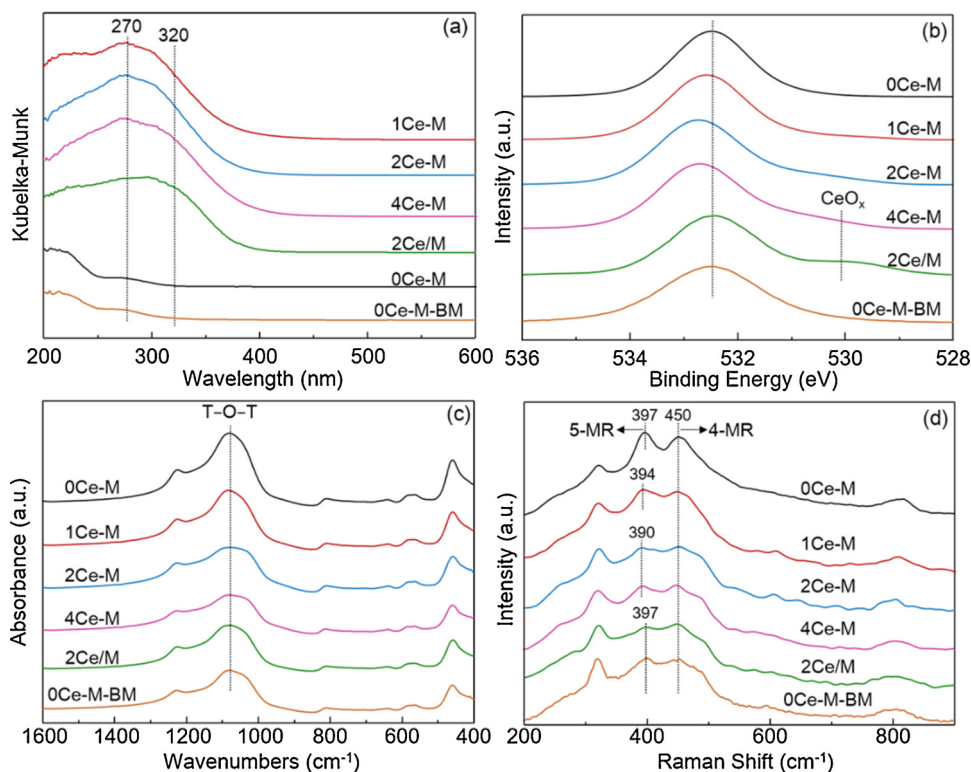


Fig. 4. (a) UV-vis spectra, (b) O 1s XPS spectra, (c) FTIR spectra in the region of framework T–O–T vibration, and (d) Raman spectra of samples.

### 3.3. Quantification of acid sites in different channels

$\text{NH}_3$ -TPD measurements were employed to explore the acidity of zeolite and the corresponding profiles are depicted in Fig. 6a. The TPD curves were deconvoluted into three peaks by Gaussian curves, denoted as  $P_1$ ,  $P_2$ , and  $P_3$ . The desorption temperature of  $P_1$ ,  $P_2$  and  $P_3$  are related to weak, moderate and strong acid sites, respectively. According to previous studies, the desorption peak of  $P_3$  in the high-temperature region is associated with framework Brønsted acid site because it completely disappears when all the framework Brønsted acid sites are replaced by  $\text{Na}^+$  [32,46,47]. The total amount of Brønsted acid sites ( $B_{\text{total}}$ ) of the samples is calculated based on the peak areas of  $P_3$  and the results are listed in Table 3. With increasing  $M_{\text{Ce}}\%$  from 0 to 2.1%,  $B_{\text{total}}$  increases significantly, suggesting that the Ce replacement is a major contributor to the increase in the number of Brønsted acid sites. It should be mentioned that when the  $M_{\text{Ce}}\%$  reached 4.1%, the  $B_{\text{total}}$  does not increase any more as a result of the collapse of MOR framework, which has been testified by BET analyses. Furthermore, the peak position of  $P_3$  for the 0Ce-M sample is about 35 °C higher in comparison to that for the Ce-incorporated samples, indicating that Ce incorporation leads to a decrease in acidic strength. On the other hand, comparing the  $B_{\text{total}}$  of 2Ce/M with 0Ce-M-BM, Ce species do not contribute to Brønsted acid sites. In contrast, Ce addition results in a slight decline in

$B_{\text{total}}$ , indicating the number of accessible Brønsted acid sites decreases, possibly owing to the partial blocking of channels by  $\text{CeO}_x$  species.

We also performed  $\text{NH}_3$ -adsorption IR to quantify the acidity of different samples. As shown in Fig. 6b, the bands at  $1430\text{ cm}^{-1}$  and  $1620\text{ cm}^{-1}$  are attributed to  $\text{NH}_3$  interacted with Brønsted and Lewis acid sites, respectively. The extinction coefficient of  $0.11\text{ cm}^2\mu\text{mol}^{-1}$  for  $1430\text{ cm}^{-1}$  and  $0.026\text{ cm}^2\mu\text{mol}^{-1}$  for  $1620\text{ cm}^{-1}$  are applied to calculate the concentration of acid sites [48]. As listed in Table 3, the amounts of Brønsted acid sites show similar values and same variation trend to the results obtained from  $\text{NH}_3$ -TPD. On the other hand, the number of Lewis acid sites is maintained at approximate  $40\text{ }\mu\text{mol/g}$  with increasing  $M_{\text{Ce}}\%$  from 0 to 2.1%, indicating that the incorporation of Ce shows negligible influence on Lewis acidity. It should be noted that the amounts of Lewis acid sites increase in 4Ce-M and 2Ce/M samples compared with that in xCe-M ( $x = 0, 1, 2$ ), resulting from excess unsaturated or extra-framework Ce species [49].

The acidity in 12-MR can be selectively measured by pyridine-adsorption IR, due to its suitable molecular kinetic diameter [12]. As shown in Fig. 6c, the bands at  $1540\text{ cm}^{-1}$  and  $1630\text{ cm}^{-1}$  are associated with pyridine adsorbed on Brønsted acid sites while the bands at  $1450\text{ cm}^{-1}$  and  $1610\text{ cm}^{-1}$  are attributed to pyridine associated with Lewis acid sites [50]. The band at  $1490\text{ cm}^{-1}$  is assigned to the overlap between Brønsted and Lewis acid sites. The quantities of Brønsted and

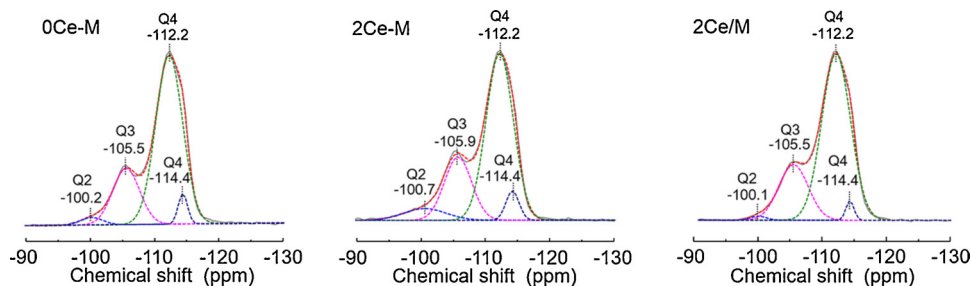


Fig. 5.  $^{29}\text{Si}$  MAS NMR spectra of samples.

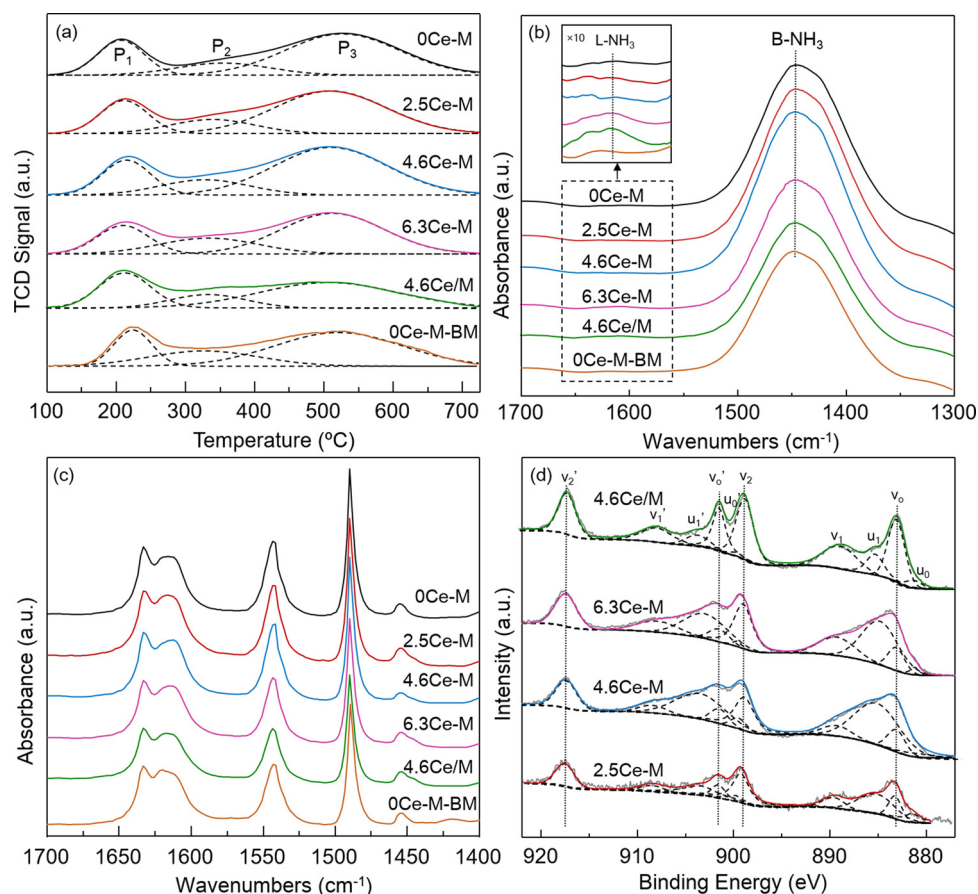


Fig. 6. (a)  $\text{NH}_3$ -TPD profiles, (b)  $\text{NH}_3$ -adsorption IR spectra, (c) pyridine-IR spectra and (d) Ce 3d XPS spectra of samples.

Lewis acid sites are calculated based on the integrated areas of the band at  $1540\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$  and their molar extinction coefficients ( $\epsilon_B = 1.67$  and  $\epsilon_L = 2.22\text{ cm}^2/\mu\text{mol}$ , respectively) calculated by Emeis [51]. As summarized in Table 3, all the samples have similar amount of Lewis acid sites in 12-MR. Combined with the results from  $\text{NH}_3$ -adsorption IR, it can be inferred that neither Lewis acidity in 8-MR nor that in 12-MR is changed after Ce incorporation for  $x\text{Ce-M}$  ( $x = 0, 1, 2$ ). Besides, with increasing the  $\text{M}_{\text{Ce}}\%$  from 0 to 2.1%, the number of Brønsted acid sites in 12-MR channel ( $\text{B}_{12\text{-MR}}$ ) is almost maintained, which is further confirmed by Pyridine-TPD (Fig. S3). Considering the gradual increase of  $\text{B}_{\text{total}}$  and nearly constant  $\text{L}_{\text{total}}$  in these three samples, the incorporated Ce species mainly affect the distribution of Brønsted acid sites in the 8-MR channel.

### 3.4. Exploring the origin of new generated Brønsted acid sites

To provide a more intuitive understanding on the Brønsted acid sites distribution, the proportion of Brønsted acid sites in 8-MR ( $\text{B}_{8\text{-MR}}\%$ ) is employed. It is calculated according to the following equation:

$$\text{B}_{8\text{-MR}}\% = \text{B}_{8\text{-MR}}/\text{B}_{\text{total}} \times 100\%$$

The calculated proportions of  $\text{B}_{8\text{-MR}}$  for 0Ce-M and 2Ce-M are 65.8% and 70.8%, respectively, which are consistent with the  $\text{B}_{8\text{-MR}}\%$  calculated from deconvolution of FTIR spectra of O–H region (Table S1 and Fig. S4). These results confirm that the regulation of Brønsted acid sites distribution is achieved through incorporation of Ce.

XPS was employed to analyze the valence states of Ce ions. As a

Table 3

The quantity of framework Al ( $\text{Al}_F$ ) and  $\text{Ce}^{3+}$  and acidity of samples ( $\mu\text{mol}\cdot\text{g}^{-1}$ ).

Sample	Quantity of elements			Quantity of acid sites					
	$\text{Al}_F^a$	$\text{Ce}^{3+b}$	$\text{Ce}^{4+b}$	$\text{B}_{\text{total}}^c$	$\text{B}_{\text{total}}^d$	$\text{L}_{\text{total}}^d$	$\text{B}_{12\text{-MR}}^e$	$\text{L}_{12\text{-MR}}^e$	$\text{B}_{8\text{-MR}}^f$
0Ce-M	1107	0	0	1218	1088	40	416	33	802
1Ce-M	1093	78	98	1289	1170	48	420	42	869
2Ce-M	1035	190	140	1425	1246	48	416	29	1009
4Ce-M	648	199	251	1134	1001	93	355	36	779
2Ce/M	1097	59	269	903	880	122	304	36	599
0Ce-M-BM	1082	0	0	1104	942	44	367	36	737

<sup>a</sup> Calculated based on ICP-OES and  $^{27}\text{Al}$  MAS NMR.

<sup>b</sup> Calculated based on ICP-OES and XPS.

<sup>c</sup> Calculated based on  $\text{NH}_3$ -TPD.

<sup>d</sup> Calculated based on IR spectra of  $\text{NH}_3$  adsorption.

<sup>e</sup> Calculated based on pyridine adsorption IR.

<sup>f</sup>  $\text{B}_{8\text{-MR}} = \text{B}_{\text{total}} - \text{B}_{12\text{-MR}}$ .

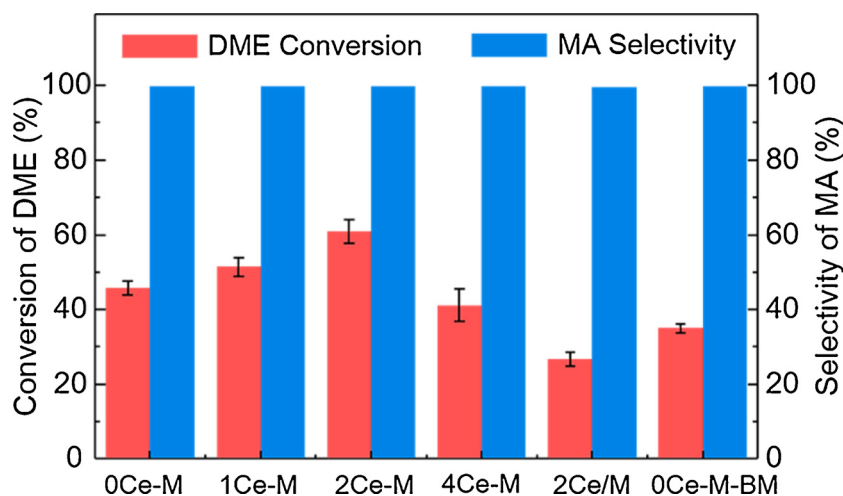


Fig. 7. DME conversion and MA selectivity of DME carbonylation over the catalyst. Reaction conditions: 200 °C, 1.5 MPa, DME/CO = 1/49, 6000 h<sup>-1</sup>.

consequence of hybridization between the O 2p states and Ce 4f levels, the Ce 3d spectra are complicated [52]. According to literature [53,54], the spectra in Fig. 6d could be deconvoluted into five Ce 3d<sub>5/2</sub>, 3/2 spin-orbit doublet peaks: two doublet for Ce<sup>3+</sup> and three doublet for Ce<sup>4+</sup>. The four peaks for Ce<sup>3+</sup> are labeled as u<sub>0</sub> (881.1 eV), u<sub>1</sub> (885.0 eV), u<sub>0</sub>' (899.5 eV) and u<sub>1</sub>' (903.4 eV). The six characteristic peaks for Ce<sup>4+</sup> are labeled as v<sub>0</sub> (882.8 eV), v<sub>1</sub> (889.4 eV), v<sub>2</sub> (898.7 eV), v<sub>0</sub>' (901.2 eV), v<sub>1</sub>' (907.5 eV) and v<sub>2</sub>' (917.1 eV). The peaks labeled as v or u are associated with 3d<sub>5/2</sub> photoemissions, while the peaks arisen from 3d<sub>3/2</sub> emission are labeled as v' and u'. The positions of the five peaks were fixed and the integrated peak area ratios of v to v', and u to u' are constrained with the value of 1.5. The decomposition and fitting of the XPS spectra were carried out using the software of XPS Peak Fit. The quantitative data of Ce<sup>3+</sup> and Ce<sup>4+</sup> amount based on XPS deconvolution and ICP are listed in Table 3. With increasing the M<sub>Ce</sub>%, the amount of Ce<sup>3+</sup> and Ce<sup>4+</sup> both increase. Nevertheless, the momentum of Ce<sup>3+</sup> slows down significantly, when the M<sub>Ce</sub>% increases from 2.1% to 4.1%. Besides, the ratio of Ce<sup>3+</sup> to Ce<sup>4+</sup> in 2Ce/M is quite different from the 2Ce-M samples, owing to the difference in Ce species between the two samples.

In the following, we took XPS together with O<sub>2</sub>-chemisorption and ICP-OES to quantitatively characterize the different Ce species. Taking 2Ce/M (prepared by ball-milling) as an example, almost all of Ce should exist as extraframework species. The deconvolution of XPS shows more than 80% Ce species are Ce<sup>4+</sup>, which indicates CeO<sub>2</sub> is the dominant species after calcination in air at 500 °C. O<sub>2</sub>-chemisorption can be used as a powerful tool to quantify Ce<sup>3+</sup> in CeO<sub>x</sub> due to the existence of oxygen vacancy. The result of O<sub>2</sub>-chemisorption shows that 51 μmol·g<sup>-1</sup> of Ce<sup>3+</sup> are present as Ce<sub>2</sub>O<sub>3</sub> that is almost equal to the total amount of Ce<sup>3+</sup> (59 μmol·g<sup>-1</sup>). Therefore, it is conclusive that most of the extraframework CeO<sub>x</sub> species in sample are CeO<sub>2</sub>, while Ce<sup>3+</sup> species are present as Ce<sub>2</sub>O<sub>3</sub>. As neither CeO<sub>2</sub> nor framework Ce<sup>4+</sup> generates Brønsted acid site, we focus on analysis of Ce<sup>3+</sup> species for one-pot synthesized samples (i.e. xCe-M).

As listed in Table 3, the total amounts of Ce<sup>3+</sup> in xCe-M (x = 1 and 2) increase with increasing M<sub>Ce</sub>%. O<sub>2</sub>-chemisorption measurement demonstrates that no O<sub>2</sub> consumption is observed on 0Ce-M and there is hardly any Ce<sub>2</sub>O<sub>3</sub> species in the other two samples (the amounts of Ce<sup>3+</sup> in Ce<sub>2</sub>O<sub>3</sub> for 1Ce-M and 2Ce-M are 2.3 and 4.7 μmol·g<sup>-1</sup> respectively). Considering that the sum of Ce<sup>3+</sup> and F<sub>Al</sub> increases proportionally with the B<sub>total</sub> (R<sup>2</sup> = 1.000), it is reasonable to infer that nearly all the Ce<sup>3+</sup> ions successfully incorporate into MOR framework during hydrothermal crystallization at low M<sub>Ce</sub>%. Besides, as the Ce<sup>3+</sup> incorporated into MOR framework is difficult to be reduced, peak at around 570 °C in H<sub>2</sub>-TPR profile is considered as the H<sub>2</sub> consumption of the extraframework CeO<sub>x</sub> species [55]. The normalized peak area of

xCe-M samples increases with the Ce content (Fig. S5), indicating the existence of more and more CeO<sub>x</sub> aggregates. Note that the 2Ce-M obtained by ball-milling exhibits the highest H<sub>2</sub> consumption. These results are in line with the other characterizations such as XPS, UV-vis etc. Moreover, the calculated ratios of framework Ce<sup>3+</sup> to CeO<sub>x</sub> (Ce<sub>F</sub>/CeO<sub>x</sub>) agree well with the semi-quantified results based on deconvolution of UV-vis spectra (Fig. S6 and Table S2), confirming the above conclusion.

In principle, in aluminosilicate zeolite, the density of Brønsted acid site is in accordance with the concentration of Al<sub>F</sub>. However, B<sub>total</sub> increases by incorporation of Ce in our case, accompanied with a decline in the quantity of Al<sub>F</sub>. Note that an increment of Ce<sup>3+</sup> species is observed along with the increase in B<sub>total</sub> and the B<sub>total</sub> is increasing in line with the sum of Al<sub>F</sub> and Ce<sup>3+</sup>, which gives a solid evidence that partial Brønsted acid sites originate from the bridging hydroxyl groups of Si-OH-Ce (similar to Si-OH-Al) due to the interaction of tetrahedral Ce<sup>3+</sup> with Si-O bonds. Thus, we conclude that the distribution of Brønsted acid site is tailored by Ce<sup>3+</sup> incorporation.

### 3.5. Catalytic performance of Ce-containing zeolite for DME carbonylation

DME carbonylation catalyzed by MOR has been reported as a typical spatial-confined reaction, in which the rate of MA formation is strictly proportional to the number of Brønsted acid sites within 8-MR channels [32,56,57]. As discussed above, the Brønsted acid sites located in 8-MR are concentrated through Ce incorporation. Thus, we investigated the catalytic performance of Ce-doped MOR catalysts in carbonylation of DME, expecting an improvement in MA yield.

Fig. 7 illustrates the initial activities of the xCe-M, 2Ce/M and 0Ce-M-BM (time on stream = 1.5 h) under the same reaction conditions, and the DME conversion versus time on stream are shown in Fig. S7. All samples exhibit an approximate selectivity greater than 98%, indicating an excellent confinement effect with respect to the 8-MR channels in MOR. An obvious deactivation is observed in all samples due to the coke deposition in 12-MR. The initial DME conversion increases from 45.7% to 61.0% as the M<sub>Ce</sub>% increases from 0 to 2.1%, owing to the enrichment of Brønsted acid sites within 8-MR channels. Besides, the DME conversion of 2Ce-M is higher than that of 0Ce-M in 7 h, confirming the enhancement of activity caused by Ce-incorporation. Further increasing the M<sub>Ce</sub>% to 4.1% results in a decreased activity, because of lower concentration of Brønsted acid sites. In addition, the DME conversion of the 0Ce-M-BM is 35.0%, apparently lower than the activity of 0Ce-M, which is due to loss of Brønsted acid sites during ball-milling process. Note that the DME conversion of the 2Ce/M sample is only 26.7%, which can be ascribed to the covering of active sites by

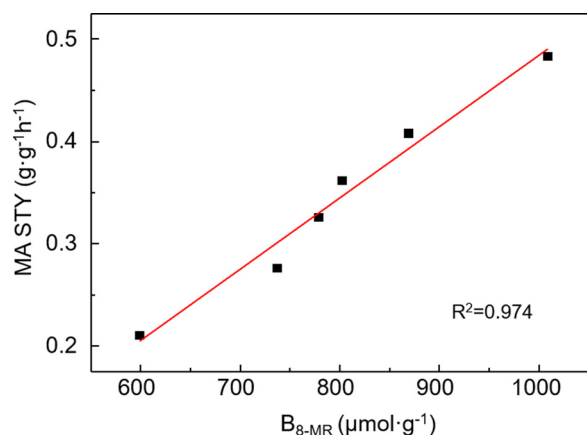


Fig. 8. Correlation between the reactivity of DME carbonylation and the amount of Brønsted acid sites in 8-MR channels.

CeO<sub>x</sub> species. For a better presentation of the relationship between activity and active sites, we plotted the STY<sub>MA</sub> against the amount of Brønsted acid sites within 8-MR (Fig. 8). As expected, a positive linear correlation is observed with  $R^2 = 0.974$ , confirming that the activity of DME carbonylation is primarily governed by the number of Brønsted acid sites within 8-MR. The comparison of activity between the 2Ce-M and published work are shown in Table S3.

In conclusion, incorporating a proper content of Ce, for instance, with a M<sub>Ce</sub>% of 2.1% in the MOR zeolite allows for the enrichment of Brønsted acid sites within 8-MR, leading to a favorable catalytic performance with respect to the carbonylation of DME.

### 3.6. Discriminating the active sites for DME carbonylation

The upshot of the above experiments provides some clues: (i) Ce incorporates into MOR framework as Ce<sup>3+</sup> species, generating new Brønsted acid sites. (ii) enrichment of Brønsted acid sites in 8-MR leads to an enhanced activity for MA formation. (iii) existence of extra-framework CeO<sub>x</sub> species causes activity loss because of deterioration of zeolitic structure. From these observations, we infer two possible promotion mechanism of Ce incorporation: a) New Brønsted acid centers in 8-MR that balance the negative charges induced by the framework Ce<sup>3+</sup> atoms (Si–OH–Ce) in tetrahedral sites function as active sites for the carbonylation of DME. b) Competitive occupancy of Ce<sup>3+</sup> and Al<sup>3+</sup> changes the distribution of Al among nonequivalent sites (i.e. 8-MR and 12-MR), enriching the bridging hydroxyl groups related to Al atoms (Si–OH–Al) in 8-MR. In this section, we endeavor to distinguish the two hypothetical promotion mechanisms by computational and experimental study.

Given that the Brønsted acid sites located at T3O33 in 8-MR channels are active for this reaction, we explore the acidic property of Si–OH–Al and Si–OH–Ce on T3O33 by calculating the bond length of O–H (d(O–H)) and deprotonation energy (shown in Table 4). Note that a longer d(O–H) and a lower E<sub>DPE</sub> correspond to greater acid strength. The calculations of all of these parameters suggest that the acidity of H-[Al]-MOR is stronger than that of H-[Ce]-MOR. This trend is in line with the observations from the NH<sub>3</sub>-TPD.

Table 4

The bond length of O–H (d(O–H)) and the deprotonation energy (DPE) of Al and Ce substituted MOR at the T3 site in 8-MR, the activation barriers and reaction energies of CO insertion to form acetyl.

Samples	d(O–H) (Å)	DPE (kcal/mol)	Activation Barriers (kcal/mol)	Reaction Energy (kcal/mol)
T3AlO33H	0.980	310.2	27.6	−13.0
T3CeO33H	0.975	316.4	37.9	−2.4

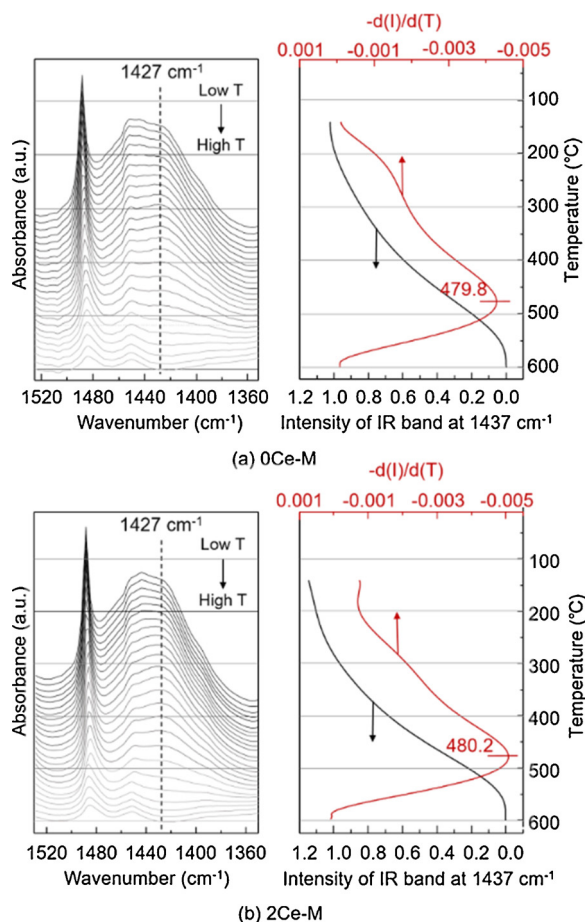


Fig. 9. IR-TPD of NH<sub>3</sub> on the (a) 0Ce-M and (b) 2Ce-M.

Although the overall properties of Brønsted acid sites in MOR have been detected by the NH<sub>3</sub> molecules, the information of Brønsted acid site in 8-MR is difficult to be distinguished from NH<sub>3</sub>-TPD profiles. Thus, in order to explore the acidity of Brønsted in 8-MR, we performed IR-TPD of NH<sub>3</sub> on the pyridine saturated MOR, in which the Brønsted acid site in 12-MR were selectively blocked by pyridine. When the pyridine saturated samples expose to NH<sub>3</sub> atmosphere at 150 °C, a band at 1427 cm<sup>−1</sup> emerges that is ascribed to the NH<sub>3</sub> molecule adsorbed on Brønsted acid site. Since the Brønsted acid sites in 12-MR have been poisoned by pyridine molecules, this band can be considered as a characteristic of the Brønsted acid site in 8-MR. With increasing the temperature from 150 °C to 600 °C under vacuum condition, the intensity of the band at 1427 cm<sup>−1</sup> decreases due to the desorption of NH<sub>3</sub> on Brønsted acid site in 8-MR [58]. The desorption rate of NH<sub>3</sub> (r<sub>NH3</sub>) is calculated by  $r_{\text{NH}_3} = -d(I)/d(T)$ , in which the I is measured from the intensity of the band at 1427 cm<sup>−1</sup>. As shown in Fig. 9, the temperatures at the desorption rate maximum of 0Ce-M and 2Ce-M are identical, indicating that the acid strength in 8-MR keeps constant even after Ce incorporation into the framework of MOR. As we mentioned above, DFT calculations reveal that the acidic strength of Si–OH–Ce is weaker than that of Si–OH–Al. Taking these observations together, we can conclude the protons in 8-MR of 2Ce-M balance the negatively charged framework induced by the presence of tetrahedrally coordinated Al<sup>3+</sup> rather than Ce<sup>3+</sup>, which are similar to the Brønsted acid sites in 0Ce-M.

In the mechanism of DME carbonylation, CO insertion into CH<sub>3</sub> to form acetyl has been identified as the rate limiting step [10]. Herein, we calculated the energy barrier for rate limiting step to explore the catalytic ability of H-[Al]-MOR and H-[Ce]-MOR. The activation barriers are 27.6 kcal/mol and 37.9 kcal/mol for H-[Al]-MOR and H-[Ce]-MOR, respectively. This indicates that the reaction occurring on a Brønsted

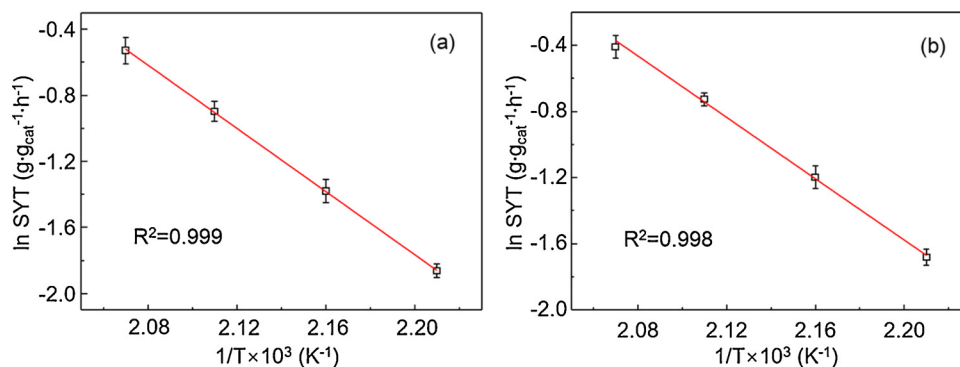


Fig. 10. Kinetic plot of the DME carbonylation catalyzed by 0Ce-M (a) and 2Ce-M (b) based on the Arrhenius equation.

acid site generated by Al is easier than that on a proton associated with Ce. On the other hand, DFT calculations show that acetyl formation is exothermic for both types of Brønsted acid sites, with a reaction energy of  $-2.4$  kcal/mol for H-[Ce]-MOR and  $-13.0$  kcal/mol for H-[Al]-MOR. This signifies that the configuration of acetyl adsorbed on H-[Al]-MOR is more stable than that on H-[Ce]-MOR. The results also suggest that a weak Brønsted acid is less active than a comparably stronger acid site [59].

Fig. 10 displays the temperature dependence of the reactivity of the DME carbonylation in the form of Arrhenius plots, which was obtained on the basis of the space time yield of MA at various temperatures ( $180^\circ\text{C}$ ,  $190^\circ\text{C}$ ,  $200^\circ\text{C}$  and  $210^\circ\text{C}$ ). As Brønsted acid sites in 12-MR are responsible for the coke formation, the initial STY on the fresh catalyst is employed to eliminate the influence of coke. The calculated apparent activation energies for the 0Ce-M and 2Ce-M catalysts are  $19.0$  kcal/mol and  $18.2$  kcal/mol, respectively. We also calculated the TOFs of 0Ce-M and 2Ce-M, and the results are  $6.1\text{ h}^{-1}$  and  $6.4\text{ h}^{-1}$ , respectively. The similarity in apparent activation energy and TOF are indicative of identical active sites for both catalysts.

In summary, comparing the experimental results with DFT calculations, we confirm that Brønsted acid sites in the 8-MR of 2Ce-M samples is also generated by  $\text{Al}^{3+}$  rather than  $\text{Ce}^{3+}$ . In other words, the new generated Brønsted acid sites (Si-OH-Ce) does not function as active sites for the carbonylation of DME and the superior activity of 2Ce-M is attributed to the enrichment of Si-OH-Al in 8-MR through Ce incorporation (Table 5).

### 3.7. Mechanistic understanding about the enrichment of Si-OH-Al in the 8-MR

In order to shed light on the mechanism of changes in Brønsted acid sites distribution in different channels, we calculated the preferred tetrahedral site for Al or Ce atom among four T sites of MOR. The

**Table 5**  
The  $E_{\text{sub}}$  of Al at different site when T1 site has been occupied by  $\text{Ce}^{3+}$  or  $\text{Al}^{3+}$  (kJ/mol).

Site	$E_{\text{subAl(T1Al)}}$	$E_{\text{subAl(T1Ce)}}$	$\Delta E_{\text{subAl(T1Al-T1Ce)}}$
T2-1	-122.2	-127.5	5.5
T4-1	-160.7	-172.5	11.8
T2-1-2	-141.4	-139.2	-2.2
T2-2	-149.6	-168.2	18.6
T3-2	-116.1	-145.6	29.5
T1-2	-179.2	-188.7	9.5
T2-3	-146.3	-128.6	-17.7
T1-3	-148.7	-155.9	7.2
T3-3	-160.8	-181.3	20.5
T1-4	-124.8	-131.9	7.1
T3-4	-158.0	-176.7	18.7
T4-4	-132.5	-136.3	3.8

relative energies of  $\text{Ce}^{3+}$  and  $\text{Al}^{3+}$  substitution in the MOR structure are shown in Table S4. The results show that both of the  $\text{Ce}^{3+}$  and  $\text{Al}^{3+}$  prefer to locate at the T1 site, consistent with the previous studies [17,60]. These results also coincide with the observations on Raman spectra that the Ce-incorporation influences the T-O-T vibration of 5-MR (T1, T2 and T4) while it does not affect the T-O-T vibration of 4-MR (T3 and T4).

To clarify the effect of Ce-incorporation on Al distribution, we set two models that T1 sites have been occupied by  $\text{Ce}^{3+}$  and  $\text{Al}^{3+}$ , respectively, and calculated the substitution energies of the second  $\text{Al}^{3+}$  at next-nearest-neighbor (NNN) T-sites of T1 on these two models ( $E_{\text{subAl(T1Ce)}}$  for  $\text{Ce}^{3+}$  substituted model and  $E_{\text{subAl(T1Al)}}$  for  $\text{Al}^{3+}$  substituted model, respectively). According to the  $E_{\text{subAl}}$  difference ( $\Delta E_{\text{subAl(T1Al-T1Ce)}}$ ) on these two models,  $\text{Ce}^{3+}$  located at T1 site leads to the easier substitution of the second  $\text{Al}^{3+}$  at most of NNN T-sites, as evidenced by  $\Delta E_{\text{subAl(T1Al-T1Ce)}} > 0$  except for T2-1-2 and T2-3 sites. Furthermore, among the NNN T sites of T1, T3 sites (i.e. T3-2, T3-3, T3-4, all in 8-MR) show the highest  $\Delta E_{\text{subAl(T1Al-T1Ce)}}$ . In other words, the occupancy of  $\text{Al}^{3+}$  on T3 sites is most significantly influenced by Ce incorporation, which results in an enrichment of Brønsted acid sites in 8-MR.

## 4. Conclusion

In summary, we successfully synthesized a series of Ce-incorporated MOR zeolites by employing a facile one-step hydrothermal route. Comparing with the ball-milling counterpart, incorporation of Ce atoms into zeolitic framework has been evidenced by multiple characterization techniques, such as lattice expansion in XRD patterns, characteristic peak of tetrahedral  $\text{Ce}^{3+}$  in UV-vis, peak shifts of O1s XPS, Raman,  $^{29}\text{Si}$  MAS NMR and broadening framework T-O-T vibrations in IR.  $\text{NH}_3$ -TPD, IR spectra of  $\text{NH}_3$  adsorption and XPS results demonstrated that Ce located at T sites in MOR as  $\text{Ce}^{3+}$  species, which created new Brønsted acid sites. The quantitative analysis of Brønsted acid sites validated that the distribution of Brønsted acid sites in the different channels (8-MR and 12-MR) of H-MOR are modulated by Ce incorporation. Incorporating a proper content of Ce, for instance, with a  $M_{\text{Ce}}\%$  of 2.1% in the MOR zeolite, is able to enrich the Brønsted acid sites in the 8-MR, whereas the number of Brønsted acid sites in 12-MR are kept unchanged. An established linear correlation between the amount of  $B_{8\text{-MR}}$  and  $\text{STY}_{\text{MA}}$  indicates that the increase of the  $B_{8\text{-MR}}$  caused by Ce isomorphous substitution is responsible for the promoted catalytic activity in DME carbonylation. Typically, a  $\text{STY}_{\text{MA}}$  of  $0.483\text{ g g}^{-1}\text{ h}^{-1}$  can be achieved at  $200^\circ\text{C}$ , which is 32.6% higher than that on 0Ce-M. Besides, the 0Ce-M and 2Ce-M exhibit almost identical Brønsted acid strength in 8-MR and the apparent active energy for DME carbonylation reaction. Since Si-OH-Al and Si-OH-Ce have distinct acidity that governs corresponding activation barrier, we attributed the improvement in activity to the enrichment of Si-OH-Al group within the 8-MR structures. Furthermore, DFT calculation revealed that

incorporation of Ce influences the occupancy of Al on T3 site significantly, which contributes to the enrichment effect on Brønsted acid sites in 8-MR. This study provides a facile approach to regulate the acidity of zeolites (not only strength but also distribution), which contributes to developing zeolite catalysts for various reactions.

## Notes

The authors declare no competing financial interest.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.117777>.

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